

PATENT APPLICATION
OF
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FOR
BICYCLIC THIOAMIDES AS ADDITIVES
FOR LUBRICATING OILS

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BICYCLIC THIOAMIDES AS ADDITIVES FOR LUBRICATING OILS

Background

This invention relates generally to bicyclic thioamides useful as additives for lubricating oils.

5 Zinc dialkyldithiophosphates (ZDDP) are widely used as lubricant additives. The principal disadvantages of these compounds are that an ash residue is produced by the zinc as the additive is consumed, and that phosphorus is known to affect the efficiency of catalytic converters in motor vehicles, thereby causing emissions problems. Cyclic compounds useful as lubricant additives are
10 disclosed in U.S. Patent No. 6,187,722. However, the compounds disclosed therein are imidazolidinethiones which are not within the scope of the present invention.

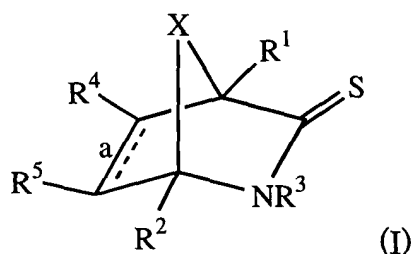
The problem addressed by this invention is to find additional non-metallic, non-phosphorus-containing oil-soluble additives for lubricating oils.

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Statement of Invention

The present invention is directed to a composition comprising:

(a) from 0.1% to 20% of at least one bicyclic thioamide of formula I:



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wherein X is O, S, NR⁶ or CR⁷R⁸; R¹, R², R⁴, R⁵, R⁷ and R⁸ independently are hydrogen, alkyl, alkenyl, aryl or aralkyl; R³ and R⁶ independently are hydrogen, alkyl, alkenyl, aryl, aralkyl, alkanoyl or aroyl; and bond "a" is a single
25 or double bond; and

(b) a lubricating oil.

The present invention is further directed to a method for improving the anti-wear characteristics of a lubricating oil by adding from 0.1% to 20% of a compound of formula I.

5 The present invention is further directed to a lubricating oil composition containing the reaction product of a compound of formula (I) with an imine; an unsaturated carboxylic acid or ester; an isocyanate or isothiocyanate; or an alkyl, alkenyl or aralkyl group bearing a leaving group.

10 The present invention is further directed to a compound having formula (IV), as depicted herein, and a composition containing the compound and a lubricating oil.

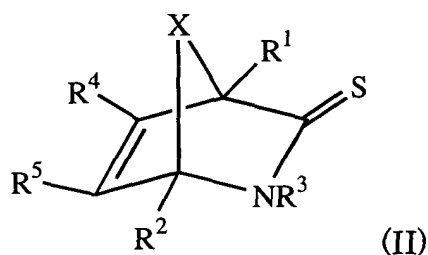
Detailed Description

15 All percentages are weight percentages based on the entire composition described, unless specified otherwise. An "alkyl" group is a saturated hydrocarbyl group having from one to twenty-two carbon atoms in a linear, branched or cyclic arrangement, and having from 0 to 2 oxygen, nitrogen or sulfur atoms. Substitution on alkyl groups of one or more halo, hydroxy, alkoxy, alkanoyl or amido groups is permitted; alkoxy, alkanoyl and amido groups may
20 in turn be substituted by one or more halo substituents. In one preferred embodiment, alkyl groups contain from two to twelve carbon atoms and from 0 to 1 oxygen, nitrogen or sulfur atoms; in another preferred embodiment, alkyl groups contain from 4 to 22 carbon atoms; in another preferred embodiment, alkyl groups contain no heteroatoms. An "alkenyl" group is an "alkyl" group in
25 which at least one carbon-carbon single bond has been replaced with a double bond. An "aryl" group is a substituent derived from an aromatic compound, including heterocyclic aromatic compounds having heteroatoms chosen from among nitrogen, oxygen and sulfur. An aryl group has a total of from five to twenty ring atoms, and has one or more rings which are separate or fused.
30 Substitution on aryl groups of one or more halo, alkyl, alkenyl, hydroxy, alkoxy, alkanoyl or amido groups is permitted, with substitution by one or more halo

groups being possible on alkyl, alkenyl, alkoxy, alkanoyl or amido groups. An “aralkyl” group is an “alkyl” group substituted by an “aryl” group. A “lubricating oil” is a natural or synthetic oil, or a mixture thereof, having suitable viscosity for use as a lubricant, e.g., as crankcase oil in an internal combustion engine, automatic transmission fluid, turbine lubricant, gear lubricant, compressor lubricant, metal-working lubricant, hydraulic fluid, etc.

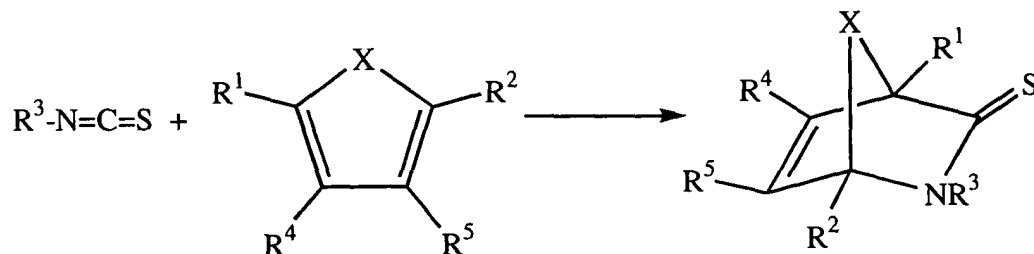
Preferably, at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 and R^8 is alkyl, alkenyl, aryl or aralkyl; more preferably at least two of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 and R^8 are alkyl, alkenyl, aryl or aralkyl. In one embodiment of the invention at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 and R^8 is aryl, aralkyl, C_4 - C_{22} alkyl or C_4 - C_{22} alkenyl; more preferably at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 and R^8 is C_4 - C_{22} alkyl or C_4 - C_{22} alkenyl; and most preferably at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 and R^8 is C_6 - C_{22} alkyl. Preferably, X is NR^6 . The composition of the present invention includes at least one compound of formula (I). In one embodiment of the invention, the composition contains at least two compounds of formula (I), and more preferably contains at least three compounds of formula (I).

In one embodiment of the invention, bond “a” is a double bond, and the compound of formula (I) can be represented by formula (II)



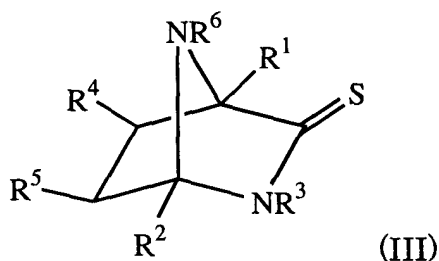
In one embodiment of the invention, a compound of formula (II) is prepared, for example, by the cycloaddition reaction of an isothiocyanate and a substituted or unsubstituted furan, thiophene, pyrrole or cyclopentadiene, as shown below in Scheme 1:

Scheme 1



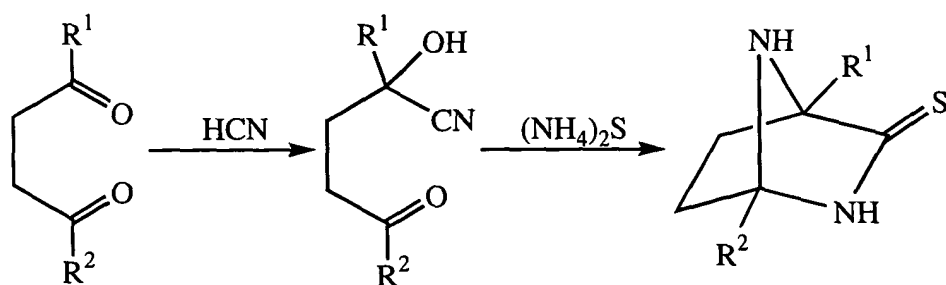
Preferably, R^3 is C_6 - C_{22} alkyl, C_6 - C_{22} alkenyl, aryl or aralkyl; more preferably R^3 is C_6 - C_{22} alkyl or aryl; most preferably R^3 is C_8 - C_{22} alkyl. Preferably, R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 and R^8 contain no heteroatoms. Preferably, at least one of R^1 , R^2 , R^3 , R^4 and R^5 is aryl, aralkyl, C_4 - C_{22} alkyl or C_4 - C_{22} alkenyl; more preferably C_6 - C_{22} alkyl or C_6 - C_{22} alkenyl; and most preferably C_{10} - C_{22} alkyl. Preferably, X is NR^6 .

In one embodiment of the invention, bond "a" is a single bond, X is NR^6 , and the compound of formula (I) can be represented by formula (III).



In one embodiment, a compound of formula (III) in which R^3 and R^6 are hydrogen, and R^4 and R^5 are hydrogen, is prepared from a 1,4-diketone, HCN and ammonium sulfide, in a two-step process, as shown below in Scheme 2:

Scheme 2



5 The NH amino group of the product optionally is further functionalized by reaction with alkyl, alkenyl, aralkyl, alkanoyl or aroyl groups having suitable leaving groups capable of being displaced by the NH group. For example, suitable leaving groups include iodide, bromide, chloride, tosylate, mesylate and triflate.

10 In a preferred embodiment of the invention, the thioamide group or a primary or secondary amino group of the compound of formula (I) is further functionalized by reaction with imines of formula $R^9N=CR^{10}R^{11}$; unsaturated carboxylic acids or esters of formula $CHR^{12}=CR^{13}COOR^{14}$; isocyanates, $R^{15}NCO$, or isothiocyanates, $R^{15}NCS$; or $R^{16}Y$; wherein R^{10} , R^{11} and R^{14} independently are
 15 hydrogen, alkyl, alkenyl, aryl or aralkyl; R^{16} is alkyl, alkenyl or aralkyl; R^{12} and R^{13} independently are hydrogen or C_1 - C_4 alkyl; R^9 and R^{15} independently are alkyl, alkenyl, aryl or aralkyl; and Y is a suitable leaving group capable of being displaced by the nitrogen or the sulfur of a thioamide group, or by a primary or
 20 secondary amine nitrogen. For example, suitable leaving groups include iodide, bromide, chloride, tosylate, mesylate or triflate. Functionalization of the thioamide group can occur on the thioamide nitrogen or the thioamide sulfur, provided of course that the thioamide nitrogen bears at least one hydrogen. The product also can be a mixture of the compound functionalized on the nitrogen and the one functionalized on the sulfur. In compounds also having a primary or
 25 secondary amino group, functionalization also may occur solely or partially on the amino group.

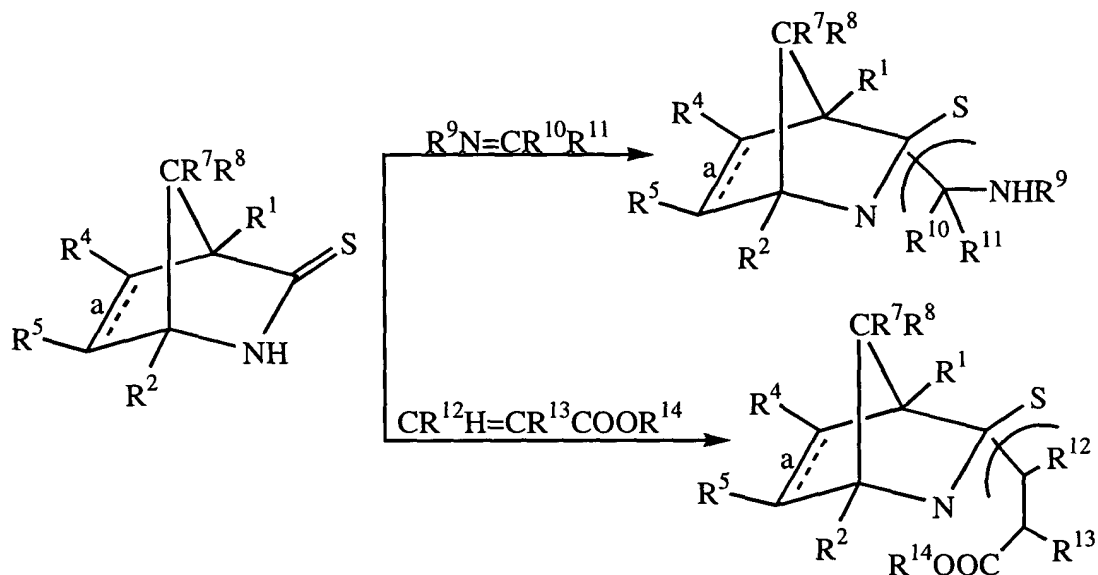
Preferably, R^{12} and R^{13} independently are hydrogen or methyl.

Preferably, the compound of formula $CHR^{12}=CR^{13}COOR^{14}$ is an alkyl or aralkyl acrylate having $R^{12}=R^{13}=H$ and $R^{14}=\text{alkyl or aralkyl}$; or a methacrylate ester having $R^{12}=H$ and $R^{13}=CH_3$; or a crotonate ester having $R^{13}=H$ and $R^{12}=CH_3$.

- 5 Preferably, R^{12} is hydrogen. Preferably, R^{14} is alkyl or aralkyl, most preferably C_4-C_{22} alkyl. Preferably, R^{15} is aryl, aralkyl or alkyl; most preferably C_8-C_{22} alkyl. Preferably, R^9 is $C_{12}-C_{22}$ alkyl. In one embodiment, R^9 is derived from an unsubstituted $C_{16}-C_{22}$ alkyl amine, R^9NH_2 , preferably one which is an oil-soluble amine. In one embodiment, the alkyl amine is a tertiary alkyl primary amine,
10 i.e., a primary amine in which the alkyl group is attached to the amino group through a tertiary carbon. Examples of commercially available tertiary alkyl primary amines are the PrimeneTM amines available from Rohm and Haas Company, Philadelphia, PA. Preferably, R^{10} and R^{11} independently are alkyl or hydrogen. In a preferred embodiment of the invention, $R^9N=CR^{10}R^{11}$ is a
15 formaldehyde imine, $R^9N=CH_2$. Preferably, R^{16} is C_4-C_{22} alkyl, C_4-C_{22} alkenyl or aralkyl; more preferably C_6-C_{22} alkyl or C_6-C_{22} alkenyl; and most preferably C_8-C_{22} alkyl.

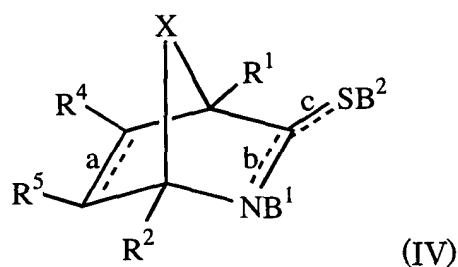
- As an example, the reaction of the compound of formula (I) in which X is CR^7R^8 , R^3 is hydrogen, and none of R^1 , R^2 , R^4 , R^5 , R^7 and R^8 contains a primary
20 or secondary amine nitrogen, with an imine and an acrylate is illustrated below in Scheme 3.

Scheme 3



- 5 The compound resulting from functionalization of the thioamide group, or an NR^6 group, with $\text{R}^6=\text{H}$, in the compound of formula (I) in which X is CR^7R^8 , O , S or NR^6 , wherein R^6 is B^3 , alkyl, alkenyl, aryl or aralkyl; R^3 is hydrogen; and none of R^1 , R^2 , R^4 , R^5 , R^6 , R^7 and R^8 contains a primary or secondary amine nitrogen, can be represented by formula (IV).

10



- wherein bonds b and c are single or double bonds, provided that one of b and c is a single bond and the other is a double bond; at least one of B^1 , B^2 and B^3 is
- 15 $-\text{CR}^{12}\text{H}-\text{CR}^{13}\text{H}-\text{COOR}^{14}$, $-\text{CR}^{10}\text{R}^{11}\text{NHR}^9$, $-\text{C}(\text{O})\text{NHR}^{15}$, $-\text{C}(\text{S})\text{NHR}^{15}$ or R^{16} ; when one of B^1 and B^2 is $-\text{CR}^{12}\text{H}-\text{CR}^{13}\text{H}-\text{COOR}^{14}$, $-\text{CR}^{10}\text{R}^{11}\text{NHR}^9$, $-\text{C}(\text{O})\text{NHR}^{15}$, $-\text{C}(\text{S})\text{NHR}^{15}$ or R^{16} , then the other is absent. When B^1 is present, bond "c" is a double bond; and when B^2 is present, bond "b" is a double bond. Preferably, at

least one of B¹, B² and B³ is -CR¹²H-CR¹³H-COOR¹⁴, -CR¹⁰R¹¹NHR⁹, -C(O)NHR¹⁵ or -C(S)NHR¹⁵. Analogous structures exist for the compounds resulting from functionalization of compounds having a primary or secondary nitrogen atom as part of an "R" substituent, in which functionalization may occur on the primary or secondary nitrogen atom, as well as on the NR⁶ group if R⁶=H, or the thioamide nitrogen or sulfur.

Preferably, the compound(s) of formula (I) is present in a lubricating oil in a total amount of at least 0.2%, more preferably at least 0.3%, and most preferably at least 0.4%. Preferably, the compound(s) of formula (I) is present in a lubricating oil in a total amount no greater than 10%, more preferably no greater than 5%, and most preferably no greater than 2%. Preferably, the compounds are soluble at the aforementioned levels.

Optionally, other additives typically used in lubricating oils are present in the composition. Such additives include, but are not limited to, other anti-wear additives, anti-corrosion additives, dispersants, detergents, antioxidants, antifoamants, friction modifiers, seal swell agents, demulsifiers, viscosity index improvers and pour point depressants. Other anti-wear additives that can be used in combination with the compound of formula (I) include the commercial products known as ZDDP, which are zinc dialkyldithiophosphates. In addition to improving the anti-wear characteristics of lubricating oils, the compound of formula (I) typically also improves anti-corrosion characteristics and functions as an anti-oxidant.